Self-irradiation damage and $5f$ localization in $PuCoGa_5$

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Abstract

Understanding superconductivity in $PuCoGa_5$ presents several challenges due to the presence of local moments and self-irradiation damage. We present x-ray absorption fine structure measurements that further establish the presence of local $5f$ electrons. Moreover, these data indicate even stronger localization after the $PuCoGa_5$ sample has aged, indicating a possible mixed valent ground state of the Pu atoms. Local structure measurements on this aged sample show an astonishing amount of damage, approaching half of the material after about 2 years. This amount of damage indicates that distortions around the Frenkel defects extend beyond the nearest neighbor, and is consistent with a percolation model for the destruction of the superconducting state after sufficient damage has accumulated.

Key words: actinide alloys and materials, superconductors, crystal structure, radiation effects, EXAFS, NEXAFS, SEXAFS
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1. Introduction

The impact of the discovery of superconductivity at T_c=18.5 K in $PuCoGa_5$ [1] has been substantial, given the nearly order-of-magnitude larger T_c than any other f-electron intermetallic. Photoemission experiments on this material reveal features associated with both localized and itinerant f-electron behavior suggesting a "dual-nature" of Pu [2]. Such a dual role is also reflected in the physical properties, in which a Curie-Weiss-like magnetic susceptibility is consistent with localized behavior, while a moderate enhancement of the specific heat coefficient ($\gamma \sim$ 100 mJ/mol K^2) suggests a predominantly itinerant character of the $5f$-electrons [1].

While the nature of the $5f$ electrons remains poorly understood in this system, the radioactive nature of plutonium is thought to be at least partially responsible for the extraordinarily high upper critical field, H_{c2} ≈100 T by providing pinning centers in otherwise single crystalline samples. Jutier and co-workers have been studying the effects of self-irradiation damage on $PuCoGa_5$ using various isotope mixtures and spiking some material with, for instance, ^{241}Am to accelerate the damage. They have found that in samples using mostly ^{239}Pu, T_c decreases $\sim$ 0.2 K/month [3], the estimated H_{c2} peaks above 120 T after about a year [3], and that the electronic mean-free path follows a predictable trend with increasing damage [4].

The study of radiation damage in materials has a long and voluminous history [5]. The early work of Kinchin and Pease (KP) [6], however, remains widely used, and is, in fact, the basis of damage calculations in the TRIM code [7,8]. In this model, each atomic site has an associated displacement threshold energy, E_d, which is the energy required to displace

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that atom sufficiently from its lattice site such that it doesn't immediately recombine. One estimate of E_d for δ-Pu is 14 eV, based on its melting point of 953 K [5]. This value, together with several assumptions about the angle of collisions, etc., can be used together with the energy and mass of the radiated particles to determine the number of displaced atoms. Together with the ensuing vacancies, these interstitial atoms form Frenkel pair defects. For an α decay of a ^{239}Pu nucleus, the α particle has about 4 MeV of energy and, using the KP model, generates nearly 300 Frenkel pairs over a distance of nearly a micron. Most of the damage, however, is done by the recoiling ^{235}U nucleus with 86 keV, which produces nearly 2300 Frenkel pairs. These energetic particles create damage cascades that extend over nearly 10 nm. Local reconstruction of the lattice is thought to reduce the effective number of defects by as much as a factor of 10 within only a few picoseconds [9].

Measuring the structural effects of radiation damage has included such techniques as x-ray and neutron diffraction, transmission electron microscopy, Rutherford backscattering, electrical resistivity, and other techniques. Although all of these methods are sensitive to various aspects of the structural disorder, the extended x-ray absorption fine-structure (EXAFS) technique offers several advantages, and hence has recently been a technique of choice for quantifying damage in materials, including plutonium alloys [10] and potential high-level waste forms [11,12]. The EXAFS technique exhibits certain strengths. First, EXAFS provides radial distribution function information around the absorbing atomic species with good resolution and pair-distance distribution widths that are accurate within about 5%. Because the data is normalized to the core absorption edge, the data provides an average per absorbing atom, and is therefore equally sensitive to amorphous regions as to highly crystalline regions of a sample. In addition, the technique is bulk sensitive, with information depths generally exceeding several microns. Complementing these structural aspects, absorption edge data (the x-ray absorption near-edge structure, or XANES) have long been used in rare-earth-based mixed valence intermetallics to determine the degree of $4f$ electron localization. Although this technique has not been useful in actinide intermetallics due to the more extended nature of the light actinide $5f$ orbitals, such measurements may be possible in plutonium intermetallics due to the position of Pu at the transition between local and delocalized f electron behavior between the light and the heavy actinides. Finally, although the data should be acquired at a synchrotron light source, it is relatively easy to obtain even with triply-contained samples, including as a function of temperature.

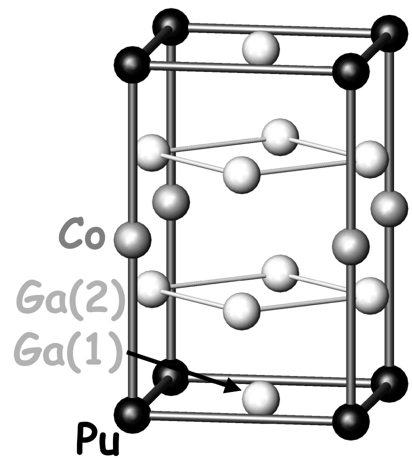

Fig. 1. Tetragonal crystal structure of $PuCoGa_5$ [1].

Here, we report XAFS measurements from the Pu L_{III}, Co K and Ga K edges on samples of $PuCoGa_5$ aged from about 2 weeks to 2 years. These data show far more self-irradiation damage than a simple Frenkel defect model suggests, indicating a large effect on the further neighbors around a given defect. Moreover, the Pu L_{III}-edge position indicates a more localized nature to the $5f$ electrons compared to those in $UCoGa_5$, as well as becoming more local with increasing radiation damage.

2. Experimental details

Single crystals of $PuCoGa_5$ (see Fig. 1 for structure) were grown by heating stoichiometric ratios of Pu and Co with excess Ga to 1100°C in a quartz-encapsulated Al_2O_3 crucible. Upon cooling overnight to 600°C, single crystals resulted, which were separated from the melt with the aid of a centrifuge. The Pu isotope mixture was determined to consist of 0.013%, 93.93%, 5.85%, 0.12% and 0.025% of ^{238}Pu through ^{242}Pu, respectively. Most of the α decays therefore are due to $^{239}\mathrm{Pu} \underset{T_{1/2}=24110y}{\longrightarrow} {}^{235}\,\mathrm{U}+\alpha$, with a significant contribution from $^{240}\mathrm{Pu} \underset{T_{1/2}=6563y}{\longrightarrow} {}^{236}\,\mathrm{U}+\alpha$. This sample therefore generates about 3.43×10^{-5} α decays per Pu per year.

The samples were ground and passed through a

32 μm sieve. About 8 mg of this powder were mixed with dried boron nitride and packed into a slot in an aluminum frame. The material was triply contained with epoxy- and indium-wire- sealed kapton widows, and placed into a LHe flow cryostat at the Stanford Synchrotron Radiation Laboratory (SSRL). Data were collected on beamlines 10-2 and 11-2 over the course of two years, generally using double Si(220) monochromator crystals. Some form of harmonic rejection was employed, either with a Rh-coated mirror, detuning the crystals, or both. Data were generally collected both in transmission mode and in fluorescence mode using various multiple element Ge detectors, although we only report transmission data here.

The data were analyzed using standard procedures [13] with the RSXAP analysis package [14]. In particular, the embedded atom absorption μ_0 was determined using a cubic spline with between 4-6 knots over the data range, which was typically about 1 keV above the absorbing threshold energy E_0, determined from the energy at the half-height of the edge.

3. Results

3.1. *Actinide L_{III}-edge XANES*

Figure 2 shows the U $L_{\rm III}$-edge data for $UCoGa_5$, an itinerant paramagnet. The data are plotted as a function of energy relative to the position of the UO_2 maximum (white line), $E_{\rm WL}$. The observed small shift is consistent with the lack of significant shift in most other measured itinerant U-based intermetallics [15].

These data contrast with $PuCoGa_5$ data in Fig. 2 which show a significant shift for $PuCoGa_5$ versus PuO_2. Moreover, the shift is noticeably larger in the two year old material (-2.45 eV) compared to the fresh sample (-1.90 eV). For comparison, the energy shift between Pu(III) and Pu(IV) aquo ion is typically about -4.4 eV [16,17]. These data strongly suggest that the aged material has a more strongly localized f orbital than that in the fresh sample, which is still very localized compared that in $UCoGa_5$. This result is not only significant because of the observation of local moment behavior, but also because it shows that such measurements are possible from Pu $L_{\rm III}$ edge XANES data from Pu intermetallics, further emphasizing the position of plutonium in the periodic table between local and delocal f-orbital states.

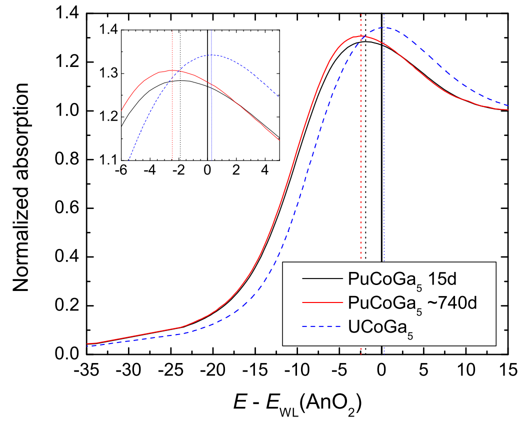

Fig. 2. Actinide $L_{\rm III}$-edge data comparing 115 samples to each other as a function of the shift of the main peak ("white line") energy, $E_{\rm WL}$ (vertical dashed lines), relative to the corresponding tetravalent actinide oxide, UO_2 or PuO_2 (solid line). The relative energy shifts are +0.30, -1.90 eV and -2.45 eV for $UCoGa_5$, 15 day old $PuCoGa_5$ and 740 day old $PuCoGa_5$. The inset shows a zoom of the white line region.

3.2. *EXAFS*

The Fourier transform (FT) of the $k^3\chi(k)$ EXAFS data from the (a) Pu $L_{\rm III}$, (b) Co K, and (c) Ga K edges are shown in Fig. 3 for both a fresh and aged sample. The fresh sample data can be fit very well to the nominal crystal structure [1,18] with narrow mean-squared displacements, σ^2's, of the pair-distance distributions of the various scattering shells up to 6 Å. The overall scale factor, S_0^2, is measured to be 0.80±0.05.

To second order, one could attempt to model the fraction of damaged sample F as

$$F = \frac{S_0^2(t)}{S_0^2(0)} + \frac{\sigma^2(t) - \sigma^2(0)}{\sigma_D^2}, \qquad (1)$$

where S_0^2 is now a function of the sample age t, $\sigma^2(t)$ is taken from the nearest neighbor to the absorbing atom, and σ_D^2 is the mean-squared displacement around a displaced ("damaged") atom. In practice, there are two problems with using such a model. First, we currently have no estimate of σ_D, and second, fits to the aged sample data, while indicating a decreasing S_0^2 as the major change in fit parameters, display a strong correlation between the S_0^2 and σ^2 parameters. Although $\sigma^2(t)$ undoubtedly is developing with time, assuming $\sigma^2(t) = \sigma^2(0)$ and $\sigma_D^2 >> \sigma^2(0)$ will still give a good estimate of the

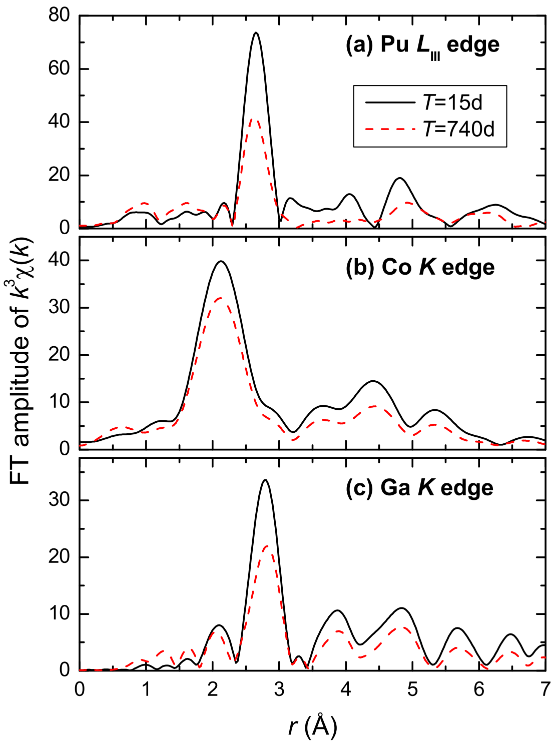

Fig. 3. The Fourier transform (FT) of the $k^3\chi(k)$ EXAFS data from the (a) Pu $L_{\rm III}$, (b) Co K, and the (c) Ga K edges are shown in Fig. 3 for both a fresh and aged sample. Transform ranges are between 2.5-16.0 Å^{-1}, 2.5-10.0 Å^{-1}, and 2.5-15.0 Å^{-1}, respectively, all Gaussian broadened by 0.3 Å^{-1}.

damaged sample fraction since $S_0^2 \sim 1/\sigma$. The effect of this assumption is to *underestimate* the damaged fraction, since weakly damaged areas still contribute to the overall amplitude.

A nice feature of this assumption is that it means we can use the amplitude of the first peak relative to that in the fresh sample's spectrum to determine the damaged fraction. This result is shown in Fig. 4 for all three absorption edges, and indicates from the Pu $L_{\rm III}$ data that more than 40% of the sample is damaged after 2 years. The fact that much of this reduction in amplitude comes from a decrease in the overall scale factor indicates that the damaged regions are nearly amorphous. Variations in this fraction with atomic species, especially for Co atoms, seems to point toward a greater tendency for light atoms to find the most stable place in the distorted structure.

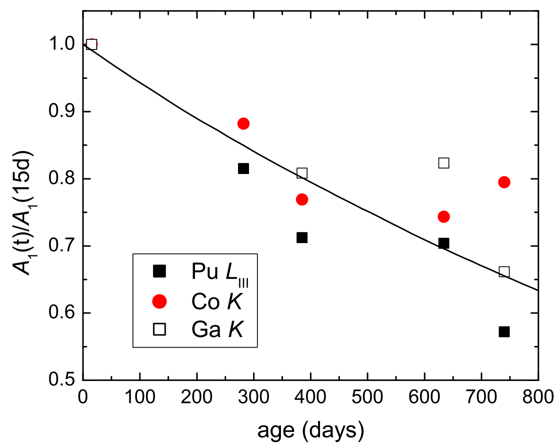

Fig. 4. The amplitude fraction of the main peak in Fig. 3 compared to a 15 day old sample for the Pu $L_{\rm III}$, Co K, and Ga K edges as a function of sample age. Also shown is a simple cubic percolation model as a guide to how the observed amplitude reduction might develop in the future. Error bars for amplitude ratios in EXAFS are typically a few percent.

4. Discussion

After two years, the results in Fig. 4 indicate more than 40% of sample has become approximately amorphized. In order for this to occur with an α-decay rate λ_α of 3.43×10^{-5} decays per Pu per year, we can calculate the number of damaged atoms per decay from

$$N_D = \frac{F_D}{(1/7)\lambda_\alpha}, \tag{2}$$

where the factor of 1/7 occurs because $1/7^{\rm th}$ of the atoms are Pu. We therefore find that about 40,000 sites are damaged as a result of each α decay, a number that is substantially larger than the estimate of 2300 Frenkel pairs per decay from δ-Pu, even if one accounts for an extra factor of two due to the interstitial/vacancy pairs in that model. The contrast is even sharper if one assumes 90% of a damaged region relaxes into the nominal lattice within some short period of time.

If one assumes that the number of Frenkel defects is roughly correct, one can in principle calculate the extent of the "damage field" around each defect from these data. For each decay, we then have 4600 total vacancies and interstitials, and with 40,000 total affected sites, between 8 and 9 atoms are strongly displaced per Frenkel defect, assuming those atoms now make no contribution to the EXAFS on average.

This would correspond roughly to the first coordination sphere. Given that only about 3% of the sites in an $\sim$8 nm cascade region are displaced directly from the recoil nucleus or the α particle, about 30% of the cascade region would be amorphized in this model. However, this estimate is likely low. If one did not assume complete amorphization, one would estimate the contribution of the damaged fraction from the increasing $\sigma^2(t)$ (as in Eq. 1). For example, one might find that the nearest-neighbor σ^2 has increased by a factor of 4, thus only accounting for half of the observed reduction in the EXAFS amplitude. The rest would be due to a smaller increase of σ^2 in the further coordination sphere, leading to a much larger number of affected sites. Since this scenario must occur to some degree, it is very likely that all of the atoms within a damage cascade have been strongly distorted from their original positions.

The observation of increasing local f character from the Pu L_{III} white line position with increasing damage is roughly consistent with the damaged fraction in the material, with about a 25% change in the white line position over two years. Moreover, it is also consistent with observations of an increase in the paramagnetic moment with sample age [4]. These observations strongly support the interpretation of the observed features in photoemission experiments as due to both local and itinerant behavior of the f electrons. This view is consistent with a Kondo coupling of the f electrons to the conduction band, since this coupling should be much weaker in the damaged regions due to the decrease in the density of states at the Fermi level, thereby causing more local moment behavior with increasing damage.

Besides the direct implications for localization both of carrier electrons and f electrons indicated by these results, the effect on superconducting properties can also be estimated. Jutier and co-workers have considered the electronic mean-free path l relative to the superconducting coherence length ξ in fresh material and conjecture that $T_c \to 0$ when $l \approx \xi$. Another important consideration is whether a conducting pathway exists across the sample. Conductivity will, of course, be impacted as soon as any damage develops, but will be more strongly impacted when damaged regions overlap enough to extend across a sample. This percolation threshold should occur with between 20-30% damaged fraction [19]. Superconductivity is not possible when the undamaged fraction is below the percolation threshold, or when the damaged fraction reached between 70-80%, a state that should occur for the present samples after $\sim$3.5-4.5 years of aging.

There are a number of important issues that are not covered by this study. The most important is the lack of work on different annealing conditions. The main sample in this study has been stored at room temperature and only taken to low temperature for between 8 and 16 hours total per experimental cycle. It would be very interesting to repeat these measurements on samples that have been stored at liquid nitrogen temperatures, and to then perform different anneals on those samples, together with other measured properties, along the lines of previous resistivity and annealing studies on δ-Pu [20]. It is also interesting to note the possible deviation of Co atoms from the main damage line in Fig. 4, and the fact that Pu atoms are consistently more damaged than Co and Ga. This difference may be due to the greater mobility of these lighter atoms in the lattice, possibly indicating their greater ability to reconstruct the original lattice positions after displacement. Studies comparing these species, and preferably other atoms in the same lattice such as Rh in $PuRhGa_5$ would help clarify this notion.

5. Conclusions

Local structural measurements on $PuCoGa_5$ demonstrate a surprising amount of self-irradiation damage after only two years since their synthesis. These results demonstrate that, unlike a simple Frenkel defect model where distortions are highly localized and defect concentrations only affect 3% of the volume within a given damage cascade, likely all of the atoms within a cascade are displaced from their original positions. Pu L_{III}-edge data demonstrate that not only are the f orbitals strongly localized in fresh $PuCoGa_5$ compared to $UCoGa_5$, but that this localization is enhanced with self-irradiation damage. Taken together, these data demonstrate the structural and electronic changes in damaged regions that are involved in destroying superconductivity in $PuCoGa_5$.

6. Acknowledgments

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